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Communications

Borato−Cyclopentadienyl Half-Sandwich Complexes. Crystal Structures of $[NEt_4][C_5H_5B(C_6F_5)_3]\cdot CH_2Cl_2$ and $[NEt_4]_2[\{C_5H_4B(C_6F_5)_3\}Zr(\mu\text{-}Cl)Cl_2]_2$

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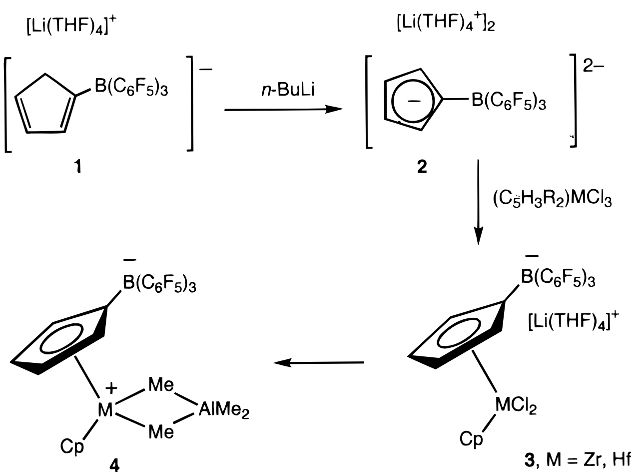
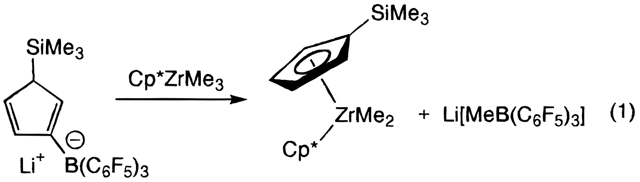
Summary: Cation exchange of $[Li(THF)_4]^+[C_5H_5B(C_6F_5)_3]^-$ *with* $[NEt_4][BF_4]$ *gives the stable, ether-free salt* $[NEt_4][C_5H_5B(C_6F_5)_3]$*, which reacts cleanly with* $Zr(NMe_2)_4$ *to afford* $[NEt_4][\{C_5H_4B(C_6F_5)_3\}Zr(NMe_2)_3]$ *in good yield. The triamide is readily converted into the crystallographically characterized dimeric trichloride* $[NEt_4]_2[\{C_5H_4B(C_6F_5)_3\}Zr(\mu\text{-}Cl)Cl_2]_2$*.*

Some time ago we described the synthesis of the cyclopentadienyl−tris(pentafluorophenyl)borate $[Li(THF)_4]^+[C_5H_5B(C_6F_5)_3]^-$ (**1**), its deprotonation by butyllithium to the dianion $[C_5H_4B(C_6F_5)_3]^{2-}$ (**2**), and the synthesis of the anionic and zwitterionic metallocene complexes **3** and **4** (Scheme 1).[1] The zwitterions **4** are attractive as alternatives to cationic metallocene-based alkene polymerization catalysts.[2,3] Very recently, Boncella et al.[4] published the synthesis of ether-free analogues of **1**, $Li[C_5H_5B(C_6F_5)_3]$ and $Li[1,3\text{-}Me_3SiC_5H_4B(C_6F_5)_3]$, but found that attempts to generate zirconium complexes by reacting these cyclopentadienylborates with $Zr(NMe_2)_4$ produced only complex mixtures, while treatment with Cp^*ZrMe_3 led to elimination of $B(C_6F_5)_3$ to give neutral metallocenes (eq 1). This report prompts

Scheme 1





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[1] Bochmann, M.; Lancaster, S. J.; Robinson, O. B. *J. Chem. Soc., Chem. Commun.* **1995**, 2081.

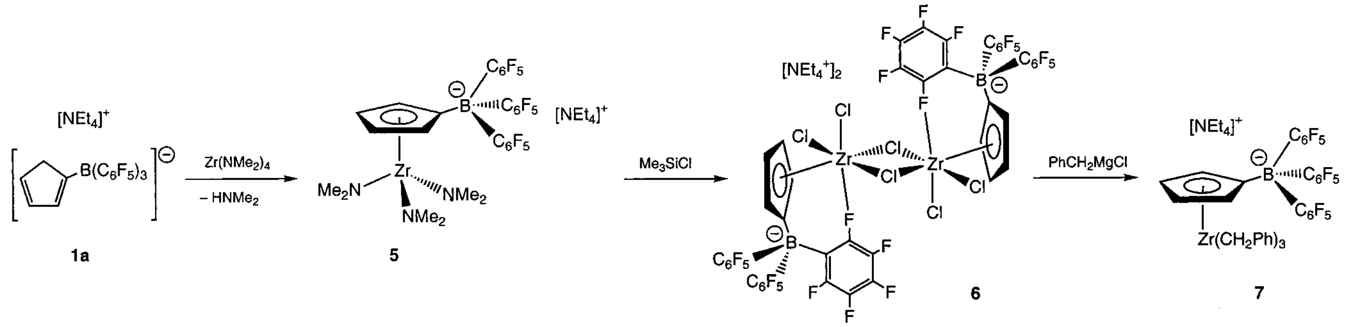
[2] Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255. Kaminsky, W. *J. Chem. Soc., Dalton Trans.* **1998**, 1413.

[3] Ruwwe, J.; Erker, G.; Fröhlich, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 80. For related zwitterionic complexes see: Song, X.; Bochmann, M. *J. Organomet. Chem.* **1997**, *545−546*, 597. Sun, Y.; Spence, R. E. v. H.; Piers, W. E.; Parvez, M.; Yap, G. P. A. *J. Am. Chem. Soc.* **1997**, *119*, 5132. Piers, W. E. *Chem. Eur. J.* **1998**, *4*, 13.

[4] Shafiq, F. A.; Abboud, K. A.; Richardson, D. E.; Boncella, J. M. *Organometallics* **1998**, *17*, 982.

S0276-7333(98)00395-1 CCC: $15.00

Scheme 2



us to describe some of our results concerning the synthesis of ether-free cyclopentadienyl–borates and the syntheses of the zirconium borato–Cp half-sandwich complexes $[\{C_5H_4B(C_6F_5)_3\}ZrX_3]^-$ (X = NMe_2, Cl, CH_2Ph) in good yields.

The reaction of LiCp with $B(C_6F_5)_3$ in THF gives $[Li(THF)_4][C_5H_5B(C_6F_5)_3]$ (**1**), which on evaporation of the solvent is isolated as a white solid. Exchange of the $[Li(THF)_4]^+$ cation is facile; treatment of **1** with $[NEt_4][BF_4]$ affords $[NEt_4][C_5H_5B(C_6F_5)_3]$ (**1a**), while the analogous reaction with $[PPh_4]Cl$ gives $[PPh_4][C_5H_5B(C_6F_5)_3]$ (**1b**).[5] These ether-free compounds are soluble in polar solvents and chlorocarbons but only sparingly soluble in toluene and insoluble in hexane.

Recrystallization of **1a** from dichloromethane gives colorless crystals of **1a**·CH_2Cl_2 suitable for X-ray diffraction. The structure of the anion in **1a** is shown in Figure 1.[6] In agreement with the NMR data, the X-ray results confirm that the 2-borato isomer is formed, in contrast to the trimethylsilyl–Cp derivative reported by Boncella et al.,[3] where the $B(C_6F_5)_3$ substituent is attached at the 3-position.

The deprotonation of cyclopentadienes with group 4 metal amides is a well-established method for the synthesis of metallocene derivatives.[7] Treatment of **1a** with 1 equiv of $Zr(NMe_2)_4$ in Et_2O at room temperature over a period of 6 h gives a clear dark yellow solution from which, on standing, the tris(amido) complex $[NEt_4][\{C_5H_4B(C_6F_5)_3\}Zr(NMe_2)_3]$ (**5**) precipitates in 60% yield (Scheme 2).[8] The complex shows characteristic ^1H NMR signals at δ 6.01 and 6.08 (2 H each) for the C_5H_4 ring and a singlet at δ 2.64 (18 H) for three NMe_2 ligands. Recrystallization from dichloromethane affords colorless needle cushions, although X-ray-quality crystals could not be obtained.

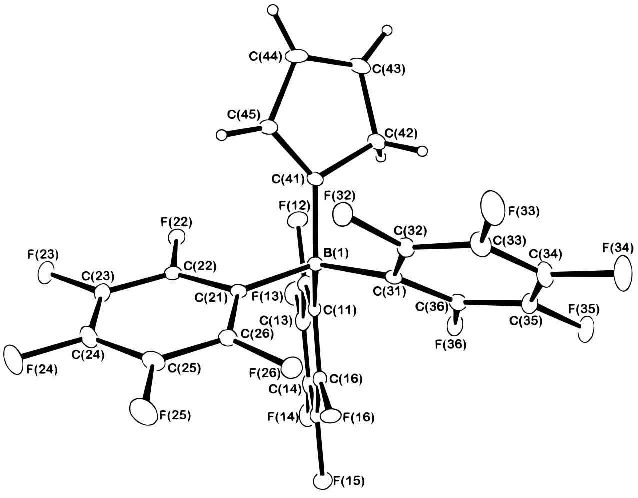


Figure 1. Structure of the $[C_5H_5B(C_6F_5)_3]^-$ anion in **1a**. Selected bond lengths (Å) and angles (deg): B–C(11), 1.660(3); B–C(21), 1.658(3); B–C(31), 1.660(3); B–C(41), 1.618(3); C(41)–C(42), 1.512(3); C(42)–C(43), 1.482(3); C(43)–C(44), 1.340(4); C(44)–C(45), 1.468(3); C(45)–C(41), 1.349(3); C(11)–B–C(21), 103.1(2); C(11)–B–C(31), 111.9(2); C(11)–B–C(41), 115.4(2); C(45)–C(41)–C(42), 106.5(2); C(41)–C(42)–C(43), 105.2(2).

Compound **5** reacts smoothly with an excess of Me_3SiCl to give the trichloride (**6**) as colorless crystals. The crystal structure[9] shows the anion in **6** to be a chloro-bridged dimer, $[NEt_4]_2[\{C_5H_4B(C_6F_5)_3\}Zr(\mu\text{-}Cl)$-

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(5) **1a**: a mixture of 43.26 g (50 mmol) of $[Li(THF)_4][C_5H_5B(C_6F_5)_3]$ and 10.9 g (50 mmol) of Et_4NBF_4 in 400 mL of CH_2Cl_2 was stirred for 3 h at room temperature. The solids were allowed to settle over 4 h before separation by filtration. Concentration of the filtrate and cooling to −20 °C overnight yielded 25.3 g of **1a**·CH_2Cl_2 (64%). Anal. Calcd for $C_{52}H_{27}BCl_2F_{15}N$: C, 48.5; H, 3.4; N, 1.8. Found: C, 49.1; H, 3.5; N, 1.5. For spectroscopic details and the synthesis of **1b** see the Supporting Information.

(6) Crystal data of **1a**·CH_2Cl_2: $C_{31}H_{25}BF_{15}N\cdot CH_2Cl_2$, fw 792.26, monoclinic, space group $P2_1/c$, $a = 8.9303(7)$ Å, $b = 24.383(2)$ Å, $c = 15.5493(13)$ Å, $\beta = 98.942(6)°$, $V = 3344.7(5)$ Å^3, $Z = 4$, $F(000) = 1600$, 5391 independent reflections, final R1 = 0.0428, wR2 = 0.1110 ($I > 2\sigma(I)$). The structure was solved by direct methods.

(7) Hughes, A. K.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 1936. Diamond, G. M.; Rodewald, S.; Jordan, R. F. *Organometallics* **1995**, *14*, 5. Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1996**, *15*, 4030. Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1996**, *15*, 4045. Christopher, J. N.; Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1996**, *15*, 4038.

(8) **5**: 6.09 g of **1a** (8.61 mmol) and 2.54 g of $Zr(NMe_2)_4$ (9.49 mmol) were combined in a flask, and 40 mL of diethyl ether was added at room temperature. The reaction mixture was stirred for 6 h as the solids gradually dissolved to give a yellow solution. The solution was filtered to separate a small amount of insoluble material; crystallization then began immediately. Cooling to 5 °C overnight gave off-white needlelike cushions, yield 4.8 g (5.2 mmol, 60%). Anal. Calcd for $C_{37}H_{42}BF_{15}N_4Zr$: C, 47.8; H, 4.6; N, 6.0. Found: C, 47.4; H, 4.6; N, 5.8. For spectroscopic data see the Supporting Information. **6**: To a solution of 6.81 g of **5** (7.32 mmol) in 30 mL of CH_2Cl_2 was added via syringe at −78 °C 5.69 mL (44.8 mmol) of $SiClMe_3$. The reaction mixture was warmed slowly to room temperature and stirred for 6 h. A small amount of precipitate was separated by filtration before concentrating the solution to 20 mL and cooling to −20 °C to give colorless cubic crystals. Further concentration and cooling gave a second crop of crystals, combined yield 4.5 g (2.28 mmol, 62%). Anal. Calcd for $C_{62}H_{48}B_2Cl_6F_{30}N_2Zr_2\cdot 2CH_2Cl_2$: C, 38.9; H, 2.7; N, 1.4. Found: C, 39.3; H, 2.7; N, 1.6. ^1H NMR (300 MHz, CD_2Cl_2, 20 °C): δ 6.77 (br, 2H, 2,5-CpB), 6.67 (br, 2H, 3,4-CpB), 3.26 (q, 8H, $J_{HH'} = 7.3$, NCH_2CH_3), 1.30 (t, 12H, $J_{HH} = 7.3$, NCH_2CH_3). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 20 °C): δ 148.75 (d, $J_{CF} = 238.8$ Hz, *o*-C of C_6F_5), 138.78 (d, $J_{CF} = 246.5$ Hz, *p*-C of C_6F_5), 137.13 (d, $J_{CF} = 250.1$ Hz, *m*-C of C_6F_5), 125.06 (2,5-CpB), 122.23 (3,4-CpB), 52.87 (NCH_2CH_3), 7.49 (NCH_2CH_3). ^{11}B NMR (96.24 MHz, CD_2Cl_2, 20 °C): δ −15.21. ^{19}F NMR (282.39 MHz, CD_2Cl_2, 20 °C): δ −132.07 (d, $J_{FF} = 21.2$ Hz, *o*-F), −161.93 (t, $J_{FF} = 20.2$ Hz, *p*-F), −165.40 (t, $J_{FF} = 20.3$ Hz, *m*-F).

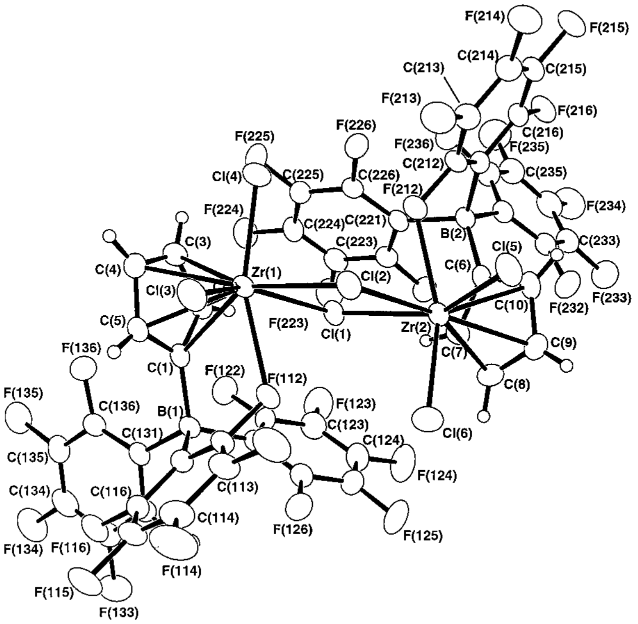
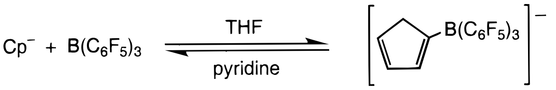


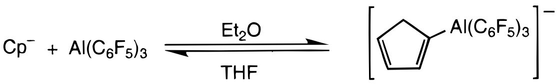
Figure 2. Structure of the anion in **6**·$2CH_2Cl_2$. Selected bond lengths (Å) and angles (deg): Zr(1)−Cl(1), 2.6035(7); Zr(1)−Cl(2), 2.503(3); Zr(1)−Cl(3), 2.503(3); Zr(1)−Cl(3), 2.4200(8); Zr(1)−F(112), 2.441(2); Zr(2)−F(212), 2.420(2); Cl(1)−Zr(1)−Cl(2), 72.80(2); Cl(2)−Zr(1)−Cl(3), 79.81(3); Cl(2)−Zr(1)−Cl(4), 83.73(3); Cl(4)−Zr(1)−F(112), 157.20(4); Zr(1)−Cl(1)−Zr(2), 108.00(3).

$Cl_2]_2$ (Figure 2), despite the very significant bulk of the $-B(C_6F_5)_3$ substituents. If one assumes one coordination site to be occupied by the Cp ligand, Cp and the four Cl ligands around zirconium occupy five positions of a distorted octahedron, which is completed by a close contact between zirconium and one of the ortho-F atoms of the C_6F_5 groups. The average Zr···F distance of 2.430(2) Å is comparable to similar Zr···F interactions in $(C_5Me_5)Zr(C_6F_5)\{\eta^4\text{-}C_4H_5B(C_6F_5)_2\}$ (2.4292(15) Å)[10] and $Cp_2Zr\{\eta^3\text{-}C_4H_6B(C_6F_5)_3\}$ (2.423(3) Å).[11]

The reaction of **1a** with $Zr(CH_2Ph)_4$ in diethyl ether gives $CpZr(CH_2Ph)_3$ and $[NEt_4][PhCH_2B(C_6F_5)_3]$, while the same reaction in toluene leads to a mixture of $CpZr(CH_2Ph)_3$ with minor quantities of $NEt_4[\{C_5H_4B(C_6F_5)_3\}Zr(CH_2Ph)_3]$ (**7**). This behavior is readily understood by considering the formation of $[C_5H_5B(C_6F_5)_3]^-$ from Cp^- and $B(C_6F_5)_3$ as an equilibrium reaction which may be reversed under certain conditions. For example, while in THF the formation of $[C_5H_5B(C_6F_5)_3]^-$ from Cp^- and $B(C_6F_5)_3$ is essentially quantitative, the addition of pyridine gives Cp^- and py·$B(C_6F_5)_3$ (eq 2). The corresponding aluminate anion $[C_5H_5Al(C_6F_5)_3]^-$ is even more labile, and its formation is already reversed by the addition of THF to diethyl ether solutions (eq 3). The displacement of Cp^- from the Cp-borate is of course no longer possible once **1** has been deprotonated to the dianion **2** or the Cp ring is coordinated to the metal.



(2)



(3)

Complex **7** is obtained in much higher yield (55%) by alkylating **6** with $PhCH_2MgCl$ and is isolated as an amorphous, spectroscopically pure orange-yellow powder.[12]

In our earlier communication[1] we reported the formation of a zirconium tribenzyl species which, on the basis of spectroscopic data, was formulated as $[Li(THF)_4]^+$-$[(C_6F_5)_2B(C_5H_4)_2\{Zr(CH_2Ph)_3\}_2]^-$. Following our recent synthesis of the cyclopentadienyl−boranes $(C_6F_5)_2B$-(C_5H_5) and $(C_6F_5)_2B(C_5H_4SiMe_3)$,[13] we attempted to reproduce the synthesis of $[(C_6F_5)_2B(C_5H_5)_2]^-$ and $[(C_6F_5)_2B(C_5H_4SiMe_3)_2]^-$ as precursors to such bi-nuclear complexes. However, all attempts to isolate bis(cyclopentadienyl)−borate anions by reacting $(C_6F_5)_2B(C_5H_4R)$ (R = H or $SiMe_3$) with cyclopentadienyl anions under a variety of conditions invariably led to intractable oils and decomposition products. A reexamination of the earlier data, therefore, leads us to conclude that the compound originally described as a borato-bridged dinuclear species was in fact mononuclear $[Li(THF)_4]$-$[(C_6F_5)_3B(C_5H_4)Zr(CH_2Ph)_3]$, which has NMR parameters very close to those of **7**, with small chemical shift differences being most likely due to the presence of the different cations.

Acknowledgment. This work was supported by the Engineering and Physical Sciences Research Council.

Supporting Information Available: Text giving preparative and spectroscopic details for **1a**, **1b**, **5**, and the formation of $[C_5H_5Al(C_6F_5)_3]^-$ and tables giving crystal data and structure refinement details, atomic coordinates, displacement parameters, and bond lengths and angles for **6** (25 pages). Ordering information is given on any current masthead page.

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(9) Crystal data of **6**: $C_{62}H_{48}B_2Cl_6F_{30}N_2Zr_2\cdot 2CH_2Cl_2$, fw 1977.64, triclinic, space group $P\bar{1}$, $a = 11.345\,30(10)$ Å, $b = 18.8050(2)$ Å, $c = 18.8553(2)$ Å, $\alpha = 90.809(7)°$, $\beta = 106.220(5)°$, $\gamma = 103.812(7)°$, $V = 3736.82(7)$ Å^3, $Z = 2$, $F(000) = 1960$, 12 925 independent reflections, final R1 = 0.0374, wR2 = 0.0986 ($I > 2\sigma(I)$). The structure was solved by Patterson methods.

(10) (a) Jiménez Pindado, G.; Thornton-Pett, M.; Bowkamp, M., Meetsma, A.; Hessen, B.; Bochmann, M. *Angew. Chem.* **1997**, *109*, 2457; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2358. (b) Jiménez Pindado, G.; Thornton-Pett, M.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1997**, 3115.

(11) (a) Temme, B.; Erker, G.; Karl, J.; Luftmann, R.; Fröhlich, R.; Kotila, S. *Angew. Chem.* **1995**, *107*, 1867; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1755. (b) Karl, J.; Erker, G.; Fröhlich, R. *J. Am. Chem. Soc.* **1997**, *119*, 11165.

(12) **7**: from 1.66 g of **5** (1.7 mmol) and $PhCH_2MgCl$ (1.0 M, 10 mL) in Et_2O (30 mL, 0 °C). Extraction with CH_2Cl_2 and evaporation of the solvent gave **7** as a golden foam (1.0 g, 0.93 mmol, 55%). ^1H NMR (300 MHz, CD_2Cl_2, 20 °C): δ 7.10 (t, 6H, $J_{HH} = 6.2$ Hz, *m*-H, Ph), 6.87 (t, 3H, $J_{HH} = 7.3$ Hz, *p*-H, Ph), 6.58 (d, 6H, $J_{HH} = 7.1$ Hz, *o*-H, Ph), 6.10 (br, 2H, 2,5-CpB), 5.53 (t, 2H, $J_{HH} = 3.0$ Hz, 3,4-CpB), 2.89 (q, 8H, $J_{HH} = 7.3$ Hz, NCH_2CH_3), 1.43 (s, 6H, CH_2Ph), 1.14 (tr, 12 H, $J_{HH} = 7.3$ Hz, NCH_2CH_3). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 20 °C): δ 148.1 (d, $J_{CF} = 232.7$ Hz, *o*-C of C_6F_5), 146.55 (ipso-C of Ph), 137.74 (d, $J_{CF} = 231.4$ Hz, *p*-C of C_6F_5), 136.35 (d, $J_{CF} = 234.2$ Hz, *m*-C of C_6F_5), 128.43 (*m*-C of Ph), 126.84 (*o*-C of Ph), 121.19 (p-C, Ph), 117.06 (2,5-CpB), 115.13 (3,4-CpB), 66.72 (CH_2Ph), 52.10 (NCH_2CH_3), 6.78 (NCH_2CH_3). ^{11}B NMR (96.29 MHz, CD_2Cl_2, 20 °C): δ −14.07.

(13) Duchateau, R.; Lancaster, S. J.; Thornton-Pett, M.; Bochmann, M. *Organometallics* **1997**, *16*, 4995.